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By William M. Dehn.

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SIMPLE DEMONSTRATIONS OF THE GAS LAWS.

BY WILLIAM M. DEHN.

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The experiments usually given in textbooks to demonstrate Charles's law and Boyle's law involve pieces of apparatus so heavy or so complicated that they are unsafe or too time-consuming to be put into the hands of beginners in chemistry. That a knowledge of these laws and of the effect of aqueous vapor on gases should be developed early in chemical instruction can scarcely be denied, but almost no laboratory course for beginners gives time or attention to these demonstrations. If considered at all and apart from the study of physics, their demonstration is given in the chemical lecture and inevitably large numbers of students fail to develop a working knowledge of the individual laws or a rational conception of their joint application in the formula:

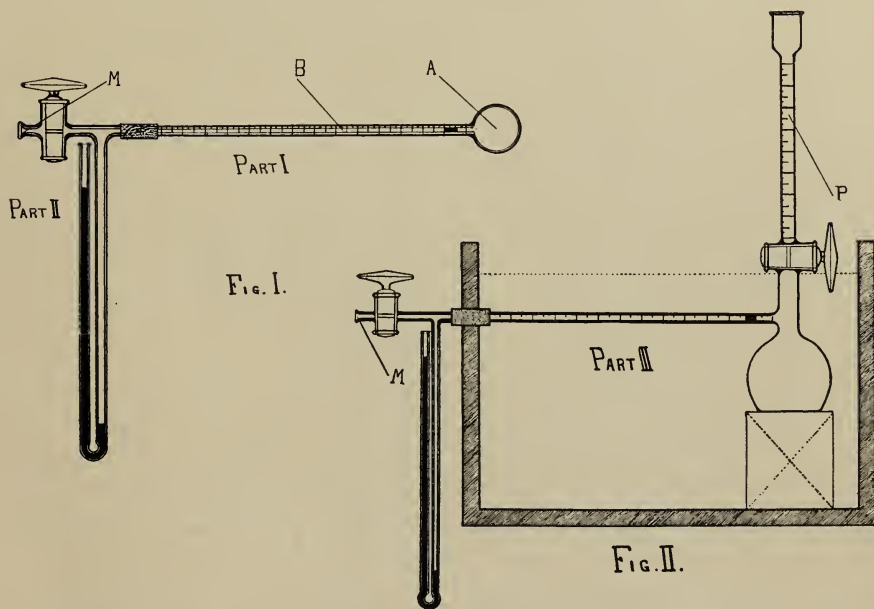
$$V = \frac{v(p-a)273}{760(273+t)}. \quad (I)$$

With the apparatus described below, involving use of the moving drop of mercury,¹ all of these effects of heat, pressure and aqueous vapor may not only be demonstrated and calculated *within one hour by the student*, but the pieces of apparatus represent small initial cost

¹ THIS JOURNAL, 29, 1052.

and minima of liability of breaking. Furthermore, these forms place in the hands of students instruments that not only admit of great accuracy but of direct *visible demonstration* of the laws. Finally these instruments not only avoid the necessity of making weighings but may in a simple manner demonstrate the *joint effect* of heat, pressure and aqueous vapor, as embodied in the above-written gas formula.

Charles's Law.—Part I consists of a calibrated bulb, A, and a graduated stem, B, whose internal diameter is less than 3 mm. Having been cleaned properly and filled with air, which must be dry or low in aqueous vapor, the mercury drop is adjusted to a position in the bulb end of the stem.¹ A rubber tube of convenient length is placed over the end of the stem and the apparatus, except the end of the rubber tube, is immersed in a pneumatic trough or a convenient form of water



bath whose temperature is near that of the room.² After adjusting the mercury drop, the temperature (t) of the bath and the volume of the air confined in the apparatus (v) are read. Hot water is then poured

¹ Of course if changes of volume at lower temperatures are to be studied, the mercury drop is adjusted near the open end of the stem. However, when working at lowered temperatures, it should be remembered that the air contained in the apparatus must be dry.

² The most simple method for the student is to place the instrument and a thermometer flat on the bottom of a pneumatic trough and to fill up with the necessary quantity of tap water. For the second readings, a beaker of hot water is prepared and added to the tap water. Increases of $20-30^{\circ}$ are usually sufficient.

into the bath and, after complete readjustment of the mercury-piston, the increased temperature (t') and the increased volume (v') are read. The mathematical relation,

$$v : v' :: (273 + t) : (273 + t'), \quad (\text{II})$$

is shown by the data to be correct or is approximated very closely.¹

Boyle's Law.—For this experiment Part II (Fig. 1) is attached to Part I and the whole apparatus is suspended on the ring of an ordinary tripod. After adjusting the mercury drop near the rubber connection of Parts I and II,² the atmospheric pressure (p) and the volume of the contained air (v) are read. Air from the lungs is then blown into the instrument at the point M, the mercury rises in the manometer, as shown in the figure, while the mercury drop moves along toward the bulb end. The stopcock is then closed and the volume of the contained air (v'') is read and the height of the mercury column in the manometer is measured and added to the atmospheric pressure as the increased³ pressure (p''). The mathematical relation,

$$v'' : v' :: p'' : p', \quad (\text{III})$$

is shown to be correct or is approximated very closely.⁴

Aqueous Vapor.—The instrument (Part III of Fig. 2) and the methods used to determine aqueous vapor are fully described in the previous contribution.⁵ Since the *volume* occupied by the aqueous vapor in air is actually determined in this experiment, its relation to the atmospheric pressure as a *partial pressure* (a) is easily developed and the true pressure of a gas containing watery vapor is seen to be $p - a$.

Almost invariably students meet with difficulty both in embodying in the gas formula the above-derived mathematical statements of the laws but also in conceiving that they really are embodied in the formula. These difficulties may be removed (1) by constant practice in successive

¹ If the *absolute temperature* is to be calculated, x in the derived equation,

$$x = \frac{v't - vt'}{v - v'},$$

shows from the experimental data close approximation to 273. Of course, the *increment of volume* for 1° C, is equal to $1/x$ and should approximate $1/273$.

² Since it is more convenient to use separate instruments for the two experiments, no readjustment of the mercury drop need be made by the student. The proper initial adjustments may be made by the instructor and the same instrument may then be used by the students for series of duplicate experiments.

³ When the mercury drop starts near the bulb end, air may be *drawn from* the apparatus and thus the effect of *reduced* pressure may be shown. In either case the height of the manometer needs to be only a little greater than 100 mm., since this is about the average pressure of air blown from or drawn into the lungs.

⁴ The average error in a class of twenty freshmen was found to be only 0.1 per cent. or an error of one part in a thousand.

⁵ THIS JOURNAL, 29, 1052-55.

application of the respective laws, (2) by development of the formula¹ from the above-derived mathematical statements of the laws, and (3) by experiments involving the simultaneous effects on gases of changed temperature, pressure and aqueous vapor pressure.

Joint Effects on Gas.—The apparatus depicted in Fig. 2 is employed to show the simultaneous effects on gas volumes of changes of temperature, pressure and aqueous vapor. When the aqueous vapor pressures (a and a') at different temperatures are taken from tables, the following method is employed: The instrument is filled with ordinary air and set up in the waterbath in the manner shown in the figure. A small measured quantity of water is run in; the volume occupied by the moist enclosed air (v), the temperature of the bath (t), the barometric pressure (p) and the aqueous pressure (a) are read. The water of the bath is gradually replaced by warmer water, until the mercury drop has moved to the limits of graduation on the manometer end of the scale; the mercury in the manometer indicates the resulting increased pressure. Should greater increased pressure be desired, sustained blowing at m produces another rise of mercury in the manometer and a simultaneous repulsion of the mercury drop along its scale. A further increase of temperature may now be made, provided the manometer can sustain an increase of pressure. The final volume (v'), temperature of the bath (t'), internal pressure (p') and aqueous pressure (a') are read. The data show that

$$\frac{v}{v'} = \frac{t(p' - a')}{t'(p - a)} \quad (\text{IV})$$

or that

$$v = \frac{v'(p' - a')t}{(p - a)t'}$$

from which, if the initial volume had been that of a dry gas at 0°C . and 760 mm., the usual gas formula may be derived.

¹ The following is given as an example of development of the gas formula. The effect on a gas of a change of temperature is shown in equation (II). Let v' be the volume at 0°C . (t') and any undetermined pressure. Solving, we have

$$v' = \frac{v(273 + t')}{273 + t} = \frac{v273}{273 + t}$$

The effect on a gas of a change of pressure is shown in equation (III). Let v'' be the volume at 760 mm. (p'') and at 0°C ., studies of changes of volume at different pressures may be made at this or any other temperature. Solving, we have

$$v' = \frac{v''p''}{p'} = \frac{v''760}{p'}$$

Equating the values of v'' , we have

$$\frac{v''760}{p'} = \frac{v273}{273 + t} \quad \text{or}$$

$$v'' = \frac{vp'273}{760(273 + t)} = \frac{v(p - a)273}{760(273 + t)}$$

in which $p - a$ is the true pressure exerted by the gas.

Should it be desired to determine experimentally all of the factors (*i. e.*, a and a') of the above equation (IV), the following method may be employed: The apparatus is first filled with dry air. After adjusting the mercury drop, the volume of the contained dry air, the temperature of the bath (t) and the barometric pressure (p) are read. A small measured quantity of water is then run in and the new volume (v) is read. From the data obtained, the aqueous pressure (a) is calculated. After v' , p' and t' have been determined by the method described above, the water of the pipette (P) is replaced by concentrated sulphuric acid and a measured quantity of the acid is run in. After the internal pressure (p') is restored by blowing at M, the volume of contained dry air is read and the original aqueous vapor pressure (a') at p' and t' is calculated.

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